STRUCTURE OF HALOGENATES OF THE TYPE A $(BO_3)_2 \cdot H_2O$

Part II. Barium Bromate Monohydrate Ba $(BrO_3)_2 \cdot H_2O$

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INTRODUCTION

IN a previous communication to these *Proceedings* (Kartha, 1952; referred to here as (I)) the details of the structure analysis and the atomic co-ordinates of one of the members of the isomorphous series of halogenate crystals A $(BO_3)_2 \cdot H_2O$, *viz.*, barium chlorate monohydrate have been reported. In continuation of these studies, the author has investigated the structure of the crystal of barium bromate monohydrate which is also isomorphous with the above series and the results are presented in this paper.

2. MORPHOLOGICAL STUDIES

Barium bromate, which is only very slightly soluble in water at room temperature, was precipitated from an aqueous solution of barium chloride by the addition of potassium bromate solution. The precipitate, which was in the form of a white powder, was washed repeatedly in warm water to remove traces of the other salts which were much more soluble than barium bromate. The final precipitate was dissolved in warm water and allowed to crystallize.

The crystals were found to be tabular in form with the *m* planes (110) most prominent. Since the results of goniometric measurements as given by different authors (Groth, 1908) were found to be different, a re-examination of the morphological data was made using a two circle optical goniometer. The measurements of the present author gave axial ratios $a:b:c = 1 \cdot 146 : 1 : 1 \cdot 215$ and these are more in accordance with those of Marignac than of either Rammelsberg or Epples. The monoclinic angle was found to be $93° 5'$.

3. UNIT CELL AND SPACE GROUP

Rotation and oscillation photographs about the crystallographic axes gave the values

$$a = 9 \cdot 1 \text{ Å}, \quad b = 8 \cdot 0 \text{ Å and } c = 9 \cdot 7 \text{ Å}$$

for the unit cell. More accurate measurements of the high order reflections from Weissenberg photographs gave the following values for the cell dimensions

$$a = 9\cdot06 \text{ Å}, \quad b = 7\cdot92 \text{ Å}, \quad \text{and} \quad c = 9\cdot66 \text{ Å}.$$

These gave the axial ratios $a : b : c = 1\cdot144 : 1 : 1\cdot219$ in good agreement with the morphological data. Taking the value $3\cdot99$ (*Handbook of Physics and Chemistry*, 1948) for the specific gravity of barium bromate crystals, the number of molecules per unit cell works out to be $3\cdot95$, *i.e.*, $Z = 4$.

From zero-level and first-level Weissenberg photographs the following systematic extinctions were observed:

Reflections hkl absent if $h + k + l$ is odd

and $h0l$ absent if either h or l is odd.

Because the crystal belongs to the monoclinic prismatic class, the only possible space group is C_{2h}^6 in the configuration $I\,2/c$. As in the case of barium chlorate monohydarte, this could be put in the standard form $C\,2/c$ as given in the *International Tables* by a suitable transformation of axes. However, the former configuration is more suitable for the purpose of structure analysis.

4. X-RAY DIFFRACTION DATA

Since the linear absorption co-efficient of the crystal is large (185 cm.^{-1}) even for Mo $K\alpha$ radiation, a very small cylindrical crystal of about $0\cdot1$ mm. radius was used in obtaining the c-axis Weissenberg photographs for the purpose of making intensity estimates. As in the case of barium chlorate monohydrate, here also the diffraction spots were recorded by the multiple film method of Robertson (1943) using three films interleaved with silver foils. The intensities were estimated by visual comparison of the diffraction spots in all the three films with standard intensity marks. Since the crystal was used after being ground to the form of a cylinder, absorption corrections were made following the method of Bradley (1935) for cylindrical Debye-Scherrer specimens. Lorentz and polarization corrections were made using the tables of Buerger and Klein (1945) for zero-level normal beam photographs and using the chart of Cochran (1948) for the higher level layers, which were recorded by the equi-inclination method. The scale and temperature factors were obtained using the method of Wilson (1942).

5. THE c-AXIS PATTERSON AND FOURIER PROJECTIONS

The symmetries and point positions for the unit cell of barium bromate monohydrate are, of course, the same as those for barium chlorate

monohydrate and they have been given in (I). Using the $hk0$ reflections, a Patterson projection was made and this is shown in Fig. 1.
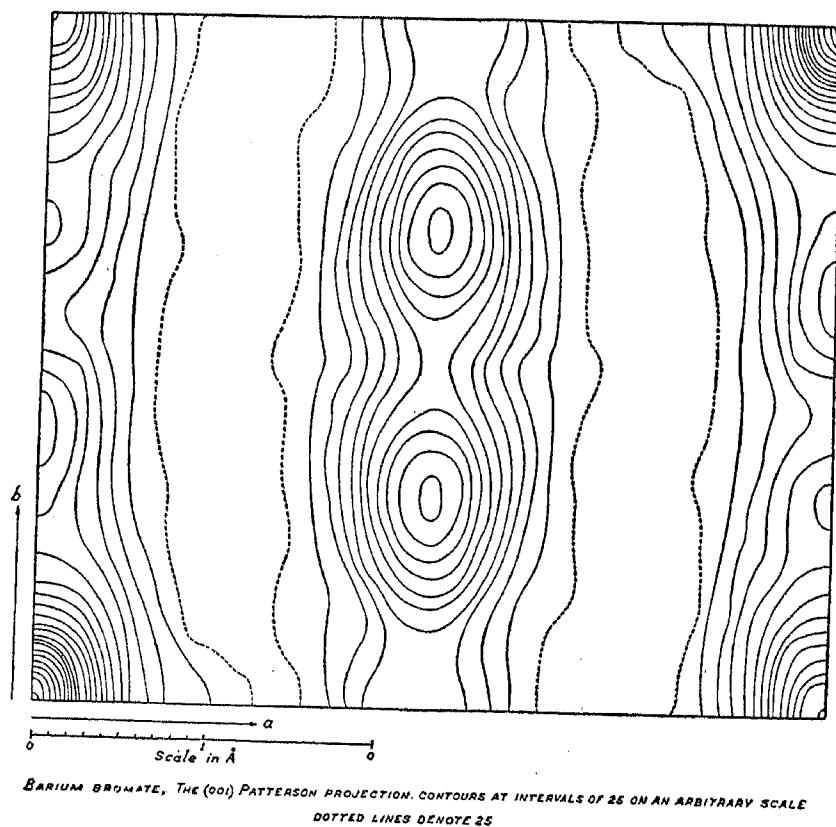

BARIUM BROMATE, THE (001) PATTERSON PROJECTION. CONTOURS AT INTERVALS OF 2S ON AN ARBITRARY SCALE
DOTTED LINES DENOTE 2S

FIG. 1

It is seen that the positions of all the important peaks could be explained by assuming that the atomic positions in the c-projection are approximately the same as in barium chlorate (I) even though the heights of the peaks suggest that an atom of much higher scattering power occupies the position of the chlorine atom. The various important peaks in the projection could be designated as shown in Table I.

However, the elongation of the Br-Br peaks along the b-axis suggests that in this case, the bromines, unlike the chlorines in the case of the chlorate, do not exactly overlap at (0·25, 0·25), in the c-projection but have slightly different b-co-ordinates.

Since the Patterson projection shows that to a first approximation the atomic co-ordinates of barium and halogens are the same both for the chlorate and bromate crystals, we see that the bromine contribution is zero for those $hk0$ reflections for which h is odd. Hence, we can assume that for these reflections the phase is entirely fixed by the sign of the barium

TABLE I

Patterson Peaks in Barium Bromate Monohydrate

| Position	Value of peak	Designation
0·00, 0·00 0·50, 0·50	580 } 580 }	All vectors $(\gamma - S)$
0·50, 0·00 0·00, 0·50	378 } 378 }	16 (Br—Br)
0·00, 0·20	211	2 (Ba—Ba)
0·00, 0·15	308	8 (Br—Ba)
0·50, 0·15 0·00, 0·15	180 } 180 }	16 (Br—O)
0·24, 0·00	146	8 (Ba—O)

contribution. In fact, the absolute structure amplitudes of barium chlorate and barium bromate are very nearly the same for these reflections. However, in the case of $hk0$ reflections with h even the eight bromine atoms make their full contribution, the sign of which is positive if $\frac{1}{2}(h + k)$ is even and negative if $\frac{1}{2}(h + k)$ is odd. Since $2f_{Br}$ is always greater than f_{Ba} we could assume that the sign is fixed by the bromine contribution for these reflections, *i.e.*, if h is even, the sign of F_{hk0} is positive or negative depending on whether $\frac{1}{2}(h + k)$ is even or odd respectively. Using the phases of reflections obtained in this way, a Fourier projection was made on the $a - b$ plane and this is shown in Fig. 2.

From Fig. 2 it is seen that in its main outlines this projection resembles the c-axis Fourier projection of barium chlorate monohydrate (I). However, the atomic positions of bariums are slightly different and the peak at (0·25, 0·25) due to overlap of two bromine atoms is more elongated in the projection. To obtain further information we have to refine the atomic co-ordinates and remove the diffraction effects around the heavy atoms. This is considered in the next section.

6. THE REFINEMENT OF ATOMIC CO-ORDINATES

The co-ordinates of the barium atoms were refined by the method of differential synthesis suggested by Booth (1946). The electron density distribution $\sigma(x, y)$ in the c-projection is represented by

$$\sigma(x, y) = \frac{1}{A} \sum_h \sum_k |F_{hk0}| \cos 2\pi \left[\left(h\frac{x}{a} + k\frac{y}{b} \right) - \alpha_{hk0} \right] \qquad (1)$$

Scale in Å
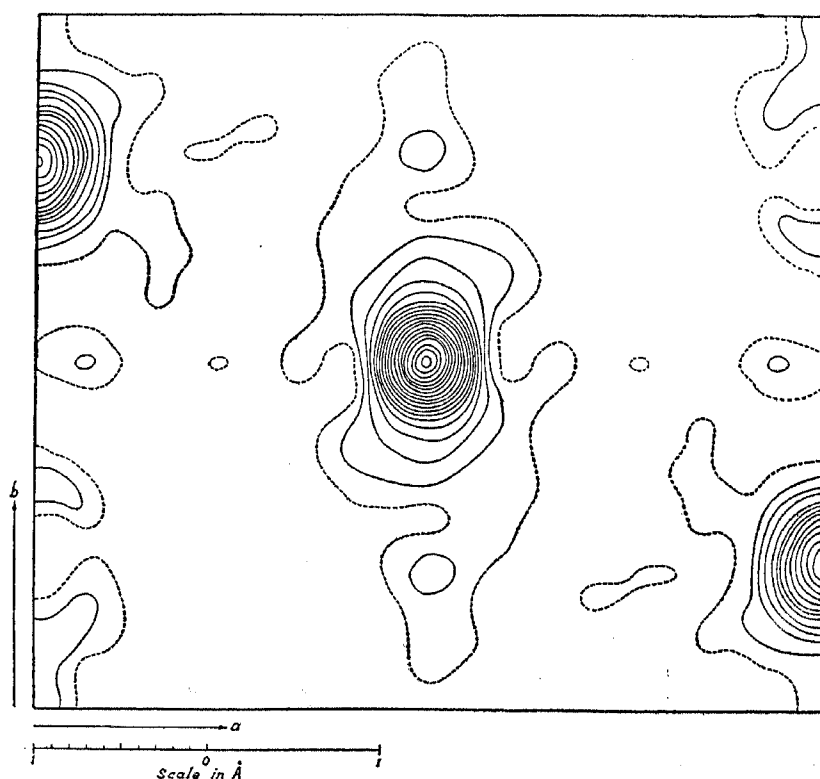
BARIUM BROMATE THE FIRST FOURIER PROJECTION ON (001). CONTOURS AT INTERVAL OF 10 e.Å⁻²
THE DOTTED LINES DENOTE 10 e.Å⁻²

FIG. 2

where A is the area of the projected unit cell. Since at the position (x_r, y_r) of maximum electron density distribution we have the conditions

$$\left(\frac{\partial\sigma}{\partial x}\right)_{x=x_r} = \left(\frac{\partial\sigma}{\partial y}\right)_{y=y_r} = 0 \tag{2}$$

we get from (1) and (2)

$$-\frac{2\pi}{Aa}\sum_h\sum_k h\left|F_{hk0}\right|\sin 2\pi\left[\left(h\frac{x_r}{a}+k\frac{y_r}{b}\right)-a_{hk0}\right]=0 \tag{3}$$

$$-\frac{2\pi}{Ab}\sum_h\sum_k k\left|F_{hk0}\right|\sin 2\pi\left[\left(h\frac{x_r}{a}+k\frac{y_r}{b}\right)-a_{hk0}\right]=0$$

If the electron density maximum, instead of being at (x_r, y_r) is actually at $(x_r + \epsilon_r{}^x, y_r + \epsilon_r{}^y)$ where ϵ is small, we get from (3) the two linear

$$A_{hh}\ \epsilon_r{}^x + A_{hk}\ \epsilon_r{}^y + A_h = 0$$

$$A_{kh}\ \epsilon_r{}^x + A_{kk}\ \epsilon_r{}^y + A_k = 0 \tag{4}$$

where

$$A_{hh} = \frac{4\pi^2}{Aa^2} \sum_h \sum_k h^2 \left| F_{hk0} \right| \cos\theta$$

$$A_{hk} = \frac{4\pi^2}{Aab} \sum_h \sum_k hk \left| F_{hk0} \right| \cos\theta$$

$$A_h = \frac{2\pi}{Aa} \sum_h \sum_k h \left| F_{hk0} \right| \sin\theta$$

$$A_{kh} = A_{hk}$$

$$A_{kk} = \frac{4\pi^2}{Ab^2} \sum_h \sum_k k^2 \left| F_{hk0} \right| \cos\theta$$

$$A_k = \frac{2\pi}{Ab} \sum_h \sum_k k \left| F_{hk0} \right| \sin\theta$$

$$\theta = 2\pi \left[\left(h\frac{x_r}{a} + k\frac{y_r}{b} \right) - a_{hk0} \right] \qquad (5)$$

Assuming the barium co-ordinates (x_r, y_r) to be $(0 \cdot 000 \, a, \ 0 \cdot 400 \, b)$, we could evaluate the quantities A_{hh}, A_{hk}, etc., of (5) and substituting these values in (4) solve for the corrections ϵ_r^x and ϵ_r^y for the barium atom. Using the data given by the $hk0$ reflections the values of ϵ^x and ϵ^y for the barium atom were calculated to be

$$\epsilon_{Ba}^y = -0 \cdot 009 \, b \quad \text{and} \quad \epsilon_{Ba}^x = 0 \cdot 0008 \, a$$

giving the refined parameters

$$x_{Ba} = 0 \cdot 0008 \, a \quad \text{and} \quad y_{Ba} = 0 \cdot 391 \, b.$$

Since the space group demands that the x-co-ordinates of the barium atom be zero, we get the final values $(0 \cdot 000, \ 0 \cdot 391)$ for the barium co-ordinates.

It was not possible to refine the bromine co-ordinates $(0 \cdot 25, \ 0 \cdot 25)$ by the method of differential synthesis for the following reasons. Firstly, $(0 \cdot 25, \ 0 \cdot 25)$ being a center of inversion, a continuous function can have a maximum at $(0 \cdot 25 + \epsilon^x, \ 0 \cdot 25 + \epsilon^y)$ only if ϵ is zero, for, otherwise the function will have two maxima having an infinitesimal separation of 2ϵ along the co-ordinate axes. As this is not possible for a continuous function there could be only one maximum corresponding to the value $\epsilon = 0$ in these cases. Secondly, due to overlap of the two bromine atoms in this region

the actual maximum could be expected to give, not the electron density maximum of either atoms separately, but only that of the combined distribution. However, the first difficulty could be got over by using co-ordinates slightly different from $(0 \cdot 25, 0 \cdot 25)$ as the starting point for the refinement. By refining the barium positions by minimization methods, where our knowledge of the electron density distribution around each atom separately could be used, the second difficulty could be overcome.

For refinement of the y-co-ordinates the function

$$R = \Sigma || RF_0 | - | F_c ||$$

was minimised by Southwell's relaxation method. Since the contribution of the bromine atoms at (x_r, y_r) to the reflection $hk0$ is $8 f_{Br} \cos 2\pi h x_r \cos 2\pi k y_r$ the condition of minimization of R gave the expression for the refinement $\epsilon_{Br}{}^y$ as

$$\epsilon_{Br}{}^y = - R \bigg/ \frac{\partial R}{\partial y_{Br}} \tag{6}$$

where

$$\frac{|| F_0 | - | F_c ||}{| F_0 | - | F_c |} \frac{\partial R}{\partial y_{Br}} = \frac{16\pi}{b} \sum_h \sum_k k f_{Br} \cos 2\pi h \frac{x_r}{a} \sin \left(2\pi k \frac{y_r}{b} - a_{hk0} \right) \tag{7}$$

Assuming that the values (x_r, y_r) for the bromine atoms are $(0 \cdot 250\, a, 0 \cdot 245\, b)$ the correction $\epsilon_{Br}{}^y$ was obtained and the value of R re-calculated using the corrected co-ordinates. Since the value of R thus calculated was actually greater than R before refinement and the correction ϵ was comparatively large, the method suggested by Booth (1949) for such cases was adopted. For this, the correction ϵ was scaled down to $0 \cdot 1$ Å and the three R values R_0, R_1 and $R_{\frac{1}{2}}$, corresponding to the three values (x_r, y_r), $(x_r, y_r + \epsilon_r)$ and $(x_r, y_r + \epsilon_r/2)$ for the barium co-ordinates, are obtained. If the curve of descent is assumed to be parabolic in nature it is easily shown that the correction $\epsilon_{min.}$ corresponding to the minimum of the function R is given by

$$\epsilon_{min} = (3 R_0 + R_1 - 4 R_{\frac{1}{2}})/ 4 (R_0 + R_1 - 2 R_{\frac{1}{2}}) \tag{8}$$

The co-ordinates of bromine and barium as well as the scale factor of the reflections were refined by this method. During the process of refinement, the reliability index R reduced from $0 \cdot 33$ to $0 \cdot 17$; the latter corresponding to the final co-ordinates $(0 \cdot 000, 0 \cdot 391)$ and $(0 \cdot 250, 0 \cdot 227)$ for the barium and bromine atoms respectively. It is interesting to note that this method also led to the same refined value $0 \cdot 391$ for the y-co-ordinate of barium as the differential synthesis method.

As explained in the case of barium chlorate monohydrate (I), a Fourier projection along c-axis free from diffraction effect was obtained by extending the series using the F_{hk0} values calculated from the bromine and barium contributions which are accurately known. The final projection thus obtained is shown in Fig. 3.

Scale in Å

Barium Bromate Final Fourier Projection on (001). Contours at intervals of 5 e.Å⁻² around oxygens and 10 e.Å⁻² elsewhere The dotted contour represents 5.e.Å⁻²
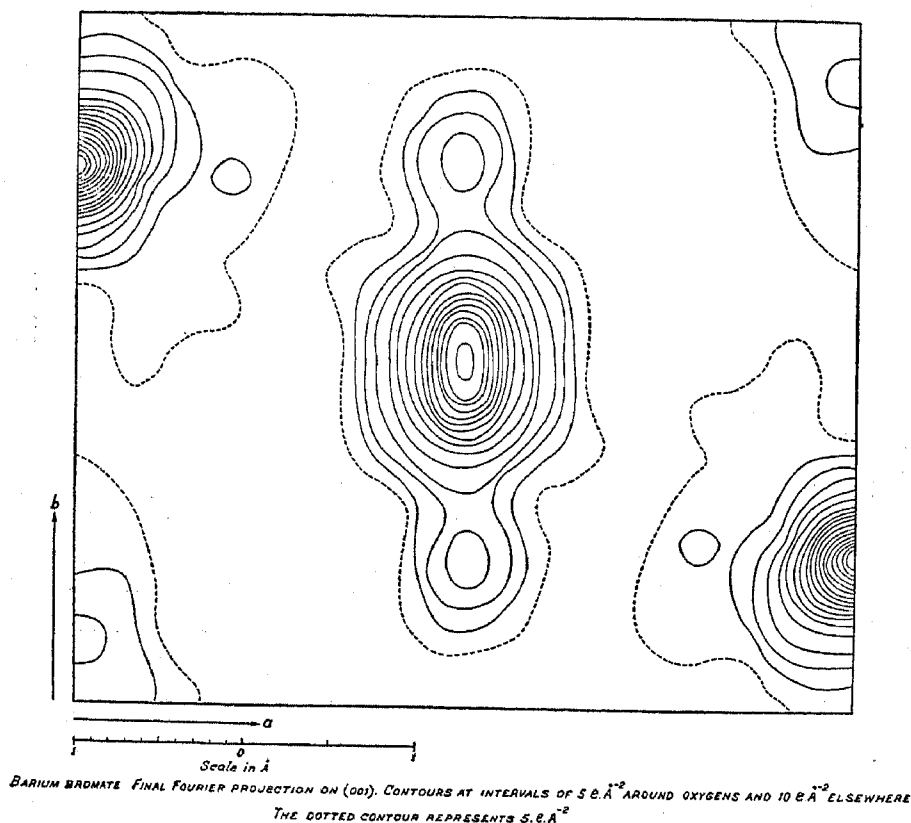
Fig. 3

Space group considerations fixed the c-co-ordinate of barium as $0 \cdot 250$. However, the c-co-ordinate of bromine is variable and this was refined by the above method using the hkl reflections and was finally fixed at $0 \cdot 550$. Since the oxygen positions could not be fixed with much accuracy due to the comparatively small scattering power of these atoms, their co-ordinates were assumed to be not much different from those in barium chlorate monohydrate in evaluating the minimization functions.

7. Atomic Co-ordinates and Discussion

The atomic co-ordinates of barium bromate monohydrate, both fractional and Ångstroms are given in Table II.

TABLE II

Atomic Co-ordinates of Barium Bromate Monohydrate

Atom		Fractional			Ångstroms		
		u	*v*	*w*	*x*	*y*	*z*
Barium	..	0·000	0·391	0·250	0·00	3·13	2·42
Bromine	..	0·250	0·227	0·550	2·27	1·82	5·31
Oxygen 1	..	0·09	0·34	0·56	0·8	2·7	5·4
Oxygen 2	..	0·25	0·10	0·66	2·3	0·8	6·3
Oxygen 3	..	0·27	0·23	0·40	2·4	1·8	3·8
Water } Oxygen }	..	0·00	0·06	0·25	0·0	0·5	2·4

As already mentioned, much accuracy is not claimed for the co-ordinates of the oxygen atoms. In Table III are given the observed and calculated structure amplitudes of the *hkO* and *hk1* reflections.

TABLE III

Observed and Calculated Structure Amplitude of
Barium Bromate Monohydrate

h	*k*	*l*	F_c	F_0	*h*	*k*	*l*	F_c	F_0
0	0	0	736	..	3	1	0	−103	89
0	2	0	−206	172	3	3	0	62	60
0	4	0	−15	<10	3	5	0	103	87
0	6	0	−140	172	3	7	0	−15	<15
0	8	0	71	58	3	9	0	−48	43
0	10	0	36	31	3	11	0	−12	14
1	1	0	−160	170	4	0	0	400	483
1	3	0	135	110	4	2	0	−111	124
1	5	0	104	118	4	4	0	−18	<10
1	7	0	7	25	4	6	0	−119	122
1	9	0	−54	45	4	8	0	60	52
1	11	0	11	<15	4	10	0	35	35
2	0	0	−88	51	5	1	0	−81	69
2	2	0	264	295	5	3	0	43	35
2	4	0	−260	225	5	5	0	84	85
2	6	0	35	25	5	7	0	3	<10
2	8	0	15	16	5	9	0	−51	44
2	10	0	27	30	5	11	0	−8	<15

TABLE III—(*Contd.*)

h	k	l	F_c	F_0	h	k	l	F_c	F_0
6	0	0	−68	75	17	1	0	−9	<15
6	2	0	160	154	17	3	0	5	<15
6	4	0	−157	145	17	5	0	9	15
6	6	0	10	25	0	1	1	−54	..
6	8	0	23	<10	0	3	1	−163	215
7	1	0	−60	60	0	5	1	42	34
7	3	0	30	25	0	7	1	63	57
7	5	0	71	63	1	0	1	0	<20
7	7	0	−10	15	1	2	1	231	224
7	9	0	−38	26	1	4	1	−38	40
8	0	0	211	218	1	6	1	4	20
8	2	0	−71	59	1	8	1	−96	132
8	4	0	−1	30	1	10	1	81	66
8	6	0	−77	79	2	1	1	154	246
8	8	0	40	47	2	3	1	−135	146
9	1	0	−56	53	2	5	1	−28	<20
9	3	0	40	23	2	7	1	108	111
9	5	0	47	60	2	9	1	10	<20
9	7	0	−4	15	2	11	1	−37	31
9	9	0	−31	−37	3	0	1	0	<20
10	0	0	−8	<10	3	2	1	77	143
10	2	0	67	65	3	4	1	129	109
10	4	0	−93	73	3	6	1	−160	176
10	6	0	12	22	3	8	1	21	<20
11	1	0	−37	32	3	10	1	−20	<20
11	3	0	25	21	4	1	1	−21	70
11	5	0	36	30	4	3	1	−139	137
11	7	0	−10	<15	4	5	1	43	30
11	9	0	−16	17	4	7	1	52	30
12	0	0	100	73	4	9	1	8	<20
12	2	0	−33	29	5	0	1	0	<20
12	4	0	−5	26	5	2	1	169	165
13	1	0	−27	19	5	4	1	−35	42
13	3	0	18	19	5	6	1	1	<20
13	5	0	22	20	5	8	1	115	78
13	7	0	−1	<15	6	1	1	−138	133
14	0	0	−5	26	6	3	1	−76	77
14	2	0	32	23	6	5	1	1	<20
14	4	0	−39	33	6	7	1	81	61
15	1	0	−13	17	7	0	1	0	<20
15	3	0	6	15	7	2	1	60	69
15	5	0	17	16	7	4	1	69	86
16	0	0	35	24	7	6	1	−119	111
16	2	0	−11	15	7	8	1	23	<20
16	4	0	0	<10	7	10	1	−18	<20

TABLE III—(Contd.)

h	k	l	F_c	F_0	h	k	l	F_c	F_0
8	1	1	−25	<20	3	8	$\bar{1}$	−106	111
8	3	1	−90	78	4	1	$\bar{1}$	−86	<20
8	5	1	41	30	4	3	$\bar{1}$	−134	154
8	7	1	26	33	4	5	$\bar{1}$	57	<20
9	0	1	0	<20	5	0	$\bar{1}$	0	<20
9	2	1	97	79	5	2	$\bar{1}$	68	84
9	4	1	−21	<20	5	4	$\bar{1}$	81	103
9	6	1	−60	71	5	6	$\bar{1}$	−150	118
10	1	1	−68	55	6	1	$\bar{1}$	−107	171
10	3	1	−38	42	6	3	$\bar{1}$	−85	55
10	5	1	−4	23	6	5	$\bar{1}$	3	<20
10	7	1	44	49	6	7	$\bar{1}$	79	77
11	0	1	0	<20	7	0	$\bar{1}$	0	<20
11	2	1	24	34	7	2	$\bar{1}$	119	134
11	4	1	41	52	7	4	$\bar{1}$	−15	<20
11	6	1	−59	71	7	6	$\bar{1}$	−5	<20
12	1	1	−2	<20	7	8	$\bar{1}$	−81	81
12	5	1	−42	49	8	1	$\bar{1}$	−22	<20
1	0	$\bar{1}$	0	<20	8	3	$\bar{1}$	−78	88
1	2	$\bar{1}$	74	86	8	5	$\bar{1}$	19	<20
1	4	$\bar{1}$	125	149	9	0	$\bar{1}$	0	<20
1	6	$\bar{1}$	−182	192	9	2	$\bar{1}$	27	43
2	1	$\bar{1}$	−208	234	9	4	$\bar{1}$	53	30
2	3	$\bar{1}$	−153	113	9	6	$\bar{1}$	−72	81
2	5	$\bar{1}$	15	23	10	1	$\bar{1}$	−50	85
2	7	$\bar{1}$	93	79	10	3	$\bar{1}$	−43	<20
3	0	$\bar{1}$	0	<20	11	0	$\bar{1}$	0	<20
3	2	$\bar{1}$	196	178	11	2	$\bar{1}$	62	63
3	4	$\bar{1}$	−53	<20	12	1	$\bar{1}$	−16	<20
3	6	$\bar{1}$	−9	<20	12	3	$\bar{1}$	−38	38

The function $R = \Sigma ||F_0| - |F_c|| / \Sigma |F_0||$ for the above reflections (about 200 in number) gave a value 0·20. This agreement between the observed and calculated values could be regarded satisfactory.

Due to the difference in ionic radii of Cl^{+5} and Br^{+5} ions the latter being appreciably larger, the unit cell dimensions and actual atomic

co-ordinates of barium bromate are slightly different from those of barium chlorate monohydrate. However, comparing the structure of the two crystals we find that the atomic arrangements in the two crystals are similar, the bromate being obtained from that of the chlorate crystal by replacing the chlorines by the bromine atoms.

SUMMARY

The crystal structure of barium bromate monohydrate has been determined and the atomic co-ordinates refined by differential synthesis and minimization methods as well as by Fourier methods. It is found that the atomic arrangement is closely similar to that in barium chlorate monohydrate.

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